TITANIUM TO BE COATED

CLEAN

FUSED SALT FLUX

ALUMINUM DIP (HEATING AND COATING)

FUSED SALT RINSE

WATER RINSE AND COOL

FINISHED WORK
This invention relates to the coating of titanium or titanium base alloys with aluminum or aluminum-base alloys and more particularly to an inexpensive process for rapidly providing an adherent coating of this type.

During recent years titanium has come into prominent industrial use but, although its physical properties are such as to be desirable in many applications, it is subject to the criticism that it is readily oxidized by air upon exposure to heat. However, an aluminum-coated titanium or titanium base alloy part, prepared in accordance with my invention, alleviates this oxidation problem and provides a part which is satisfactory for use in a great many applications.

Tubes for which my invention is particularly adapted include aluminum brazing of titanium parts, such as the joining of titanium aircraft propeller blade halves by aluminum brazing and the brazing of turbine compressor blades to the compressor hub. These parts may be first aluminum coated, and then the aluminum coating on the parts may be brazed by an aluminum alloy, preferably of lower melting point, to join the parts together. Aluminum-coated titanium compressor blades also may be advantageously used in axial-flow compressors. The last few stages of these compressors become very hot during operation, and coating them with aluminum provides excellent oxidation resistance. Moreover, aluminum bearings having titanium-base alloy backings may be satisfactorily formed in accordance with my invention. The titanium backing is first coated with aluminum or an aluminum alloy, and then the aluminum bearing is brazed to the aluminum coating. A sound joint is provided and the aluminum-alloy interface is not detrimental to the performance of these parts in the service to which they are subjected.

The present invention may also be advantageously used in the preparation of hot ingot or billet titanium stock. Coating this stock with aluminum prior to hot reduction prevents oxidation of the titanium or titanium-base alloy and renders it to be more easily formed.

A principal object of the present invention, therefore, is to provide a simple, practical and inexpensive process for coating titanium or titanium base alloys with aluminum or aluminum-base alloys. This process produces a product of high quality in which there is provided a continuous chemical bond at the interface of the aluminum coating metal and the titanium part.

Another object of my invention is to provide a titanium or titanium base alloy article which is coated with aluminum or an aluminum base alloy to greatly increase its oxidation resistance and to thereby improve the hot working properties of this part. A still further object of the invention is to provide an aluminum-coated titanium product which may be easily and securely brazed to other aluminum surfaces.

Other objects and advantages of this invention will more fully appear from the following detailed description of a preferred embodiment of the invention, which will be best understood by reference to the accompanying drawing and the following description of the preferred embodiment.

It will be understood that, by "aluminum base alloys," as hereinafter used, it is meant those aluminum alloys, including pure aluminum, which in general contain at least approximately 90% aluminum. Hence, it will also be understood that the terms "aluminum" and "aluminum base alloy," as used herein, are interchangeable and are not intended to restrict any phases of the invention to only one of these groups. Similarly, the terminology "titanium base alloy" or "titanium base metal" is meant to include pure titanium and all alloys thereof in which titanium constitutes at least 50% of the alloy.

Titanium or titanium-base alloys of any shape can be coated with pure aluminum or aluminum base alloys by the method of this invention. The process may be a continuous one if desired, especially where the metal being coated is sheet, wire or rod stock.

Titanium base alloys which may be coated in accordance with my invention include the commercially available alloys containing appreciable amounts of chromium. Typical examples of these alloys are those having the following compositions:

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<tr>
<td>Iron</td>
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<tr>
<td>Oxygen</td>
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<tr>
<td>Nitrogen</td>
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<tr>
<td>Tungsten</td>
<td>0.08</td>
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<tr>
<td>Carbon</td>
<td>0.02</td>
</tr>
<tr>
<td>Balance</td>
<td>Substantially All Titanium</td>
</tr>
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</table>

Maximum, 2.70

Similarly, as hereinafter indicated, my process is adapted for use in coating pure or "commercially pure" titanium with aluminum or an aluminum base alloy. A typical example of this latter type of titanium alloy is one consisting essentially of 0.10% iron, 0.02% nitrogen, carbon not in excess of 0.04%, traces of oxygen, and the balance substantially titanium. I have found that, in general, the alloys containing the lower percentages of titanium may be more easily coated by my process than those having a very high titanium content.

The surface of the titanium base alloy to be coated are preferably cleaned in any suitable manner prior to the actual coating operation. More consistent and uniform results are obtained if mechanical cleaning means, such as grit blasting, sand blasting, hydroblasting or vapor blasting, is employed. Other suitable cleaning treatments, such as etching by appropriate fluxes, may be employed if desired. This preliminary cleaning treatment, although recommended as a preferred step in the procedure, is not necessary in all instances.

After cleaning the surfaces of the titanium base alloy to be coated, it is immersed in a molten or fused salt bath. In accordance with my invention, the preferred method for aluminum coating a titanium base alloy is to pass an unheated titanium base metal part directly through a relatively thin layer of the fused salt which is floating on a molten aluminum or aluminum base alloy coating bath. The cold titanium base metal, in passing through the layer of activated salt flux, will become coated with a layer of the flux which may solidify, but which will remain after sufficient time of contact with the molten aluminum or aluminum alloy bath underneath the fused salt layer. An excellent coating of aluminum on a titanium base alloy may be obtained by this preferred procedure because the aluminum contacts the titanium alloy immedi-
3. After the salt is removed from the surface, and there is no opportunity for titanium oxides to form. Therefore, the salt bath must be one capable of dissolving aluminum and titanium oxides. Accordingly, it has been found that a highly satisfactory salt bath is one comprising, by weight, 37% to 57% potassium chloride (KCl), 25% to 45% sodium chloride (NaCl), 8% to 20% cryolite (Na₃AlF₆), and 0.5% to 12% aluminum fluoride (AlF₃). A bath containing essentially 47% by weight of potassium chloride, 35% by weight of sodium chloride, 12% by weight of cryolite, and 6% by weight of aluminum fluoride is a specific example of this salt bath which provides excellent results.

The bath composition usually preferred is one which will become molten when heated to a temperature of approximately 1200°F. or somewhat lower. The above specific salt bath has a melting point of approximately 1180°F. and, if desired, a small amount of lithium chloride may be added to the salt to lower the melting point thereof. For example, the addition of about 20% lithium chloride lowers the melting point of this composition to approximately 1075°F. During operation the temperature of the fused salt bath is maintained somewhat above the melting point of the aluminum or aluminum base alloy, a temperature range of the approximate 1200°F. to 1600°F. usually being satisfactory. In general, however, a temperature between 1300°F. and 1400°F. is preferred.

While in the foregoing examples the double salt Na₃AlF₆/KCl cryolite) is included in the bath, it should be understood that an equivalent amount of the component may be supplied in the form of the single salts, sodium fluoride and aluminum fluoride. However, I have found that it is essential to provide an excess of AlF₃ over that of the cryolite ratio in order to obtain the desired results.

The immersion of the titanium alloy in the described fused salt prior to immersion in the aluminum or aluminum base alloy bath will provide a clean surface on the titanium base metal part unless it is exceptionally contaminated initially, and this is a principal reason why it is usually not essential to first clean the titanium as outlined above.

The molten metal coating bath may be pure aluminum or an aluminum base alloy and, as hereinbefore indicated, this alloy preferably should contain approximately 80% or more aluminum. An aluminum base alloy which is particularly advantageous is one composed of approximately 5% to 15% silicon and the balance aluminum. This alloy has a relatively low melting temperature, i.e., eutectic at 12% silicon, and has high fluidity, both of these properties being highly advantageous in using the coating metal spelter for subsequent brazing operations, if so desired. Effective drainage of excess coating metal is obtained because of this high fluidity, particularly when protected from air during cooling by the salt flux layer. Specific examples of other appropriate aluminum base alloys include an alloy composed of 4% copper and the balance aluminum, an alloy composed of approximately 7% tin or 7% silicon and 93% aluminum, and an alloy containing 5% to 20% zinc and the balance substantially all aluminum. These specific examples are referred to merely for purposes of illustration and not of limitation.

At present it is preferred that the temperature of the aluminum or aluminum base alloy coating bath be maintained at a temperature between about 1250°F. and 1325°F. Temperatures within the approximate range of 1150°F. to 1600°F. are suitable, however, for the aluminum base alloys. Pure aluminum melts at approximately 1218°F., and consequently, when employing pure aluminum as the coating metal, aluminum and salt bath temperatures must be 1218°F. or higher. The upper temperature employed with pure aluminum as the coating metal is also approximately 1600°F.

After passing through the fused salt flux and into the molten aluminum or aluminum base alloy bath, the coated titanium or titanium base alloy part is permitted to remain in the coating bath until at least its surface reaches the melting point of the coating metal. The aluminum-coated titanium base metal part is then coated with the molten salt layer. At times there may be a tendency to form a thinner but uniform coating of aluminum or aluminum alloy than desired. Excess molten coating material can be further drained off by passing the aluminum base alloy part slowly through the molten salt during removal from the bath. Alternatively, this draining of excess coating metal may be accomplished by holding the coated part in the fused salt for a short period of time after it has been withdrawn from the coating bath. The coated titanium base alloy part, after removal, or as it is being removed from the aluminum or aluminum alloy bath, also may be rapidly vibrated or rotated or treated in other equivalent manner in order to remove excess molten or mushy coating metal. Similarly, the coated surfaces of the part may be air blasted to remove any excess coating metal without detriment to the aluminum coating.

The coated titanium or titanium base alloy part is then cooled or permitted to cool. Water or other quenching media may be employed for this purpose. The excess coating metal may be removed by washing, for example, or the coated titanium base metal part may be passed through rollers to remove the flux and to provide a desirable finish to the coated product. Cleaning or brightening of the aluminum-coated article can follow accepted commercial methods for aluminum parts. The flow sheet shown in the drawing illustrates the steps of the aforementioned process.

The procedure described above constitutes a preferred embodiment of processing in accordance with my invention. However, it is possible to obtain satisfactory coatings of aluminum or aluminum base alloys on titanium base alloys by departures from the conditions of the preferred embodiment. For example, the titanium base alloy part may be retained in the fused salt a sufficient time to heat it to or above the melting point of the aluminum or aluminum base alloy. Although, in this procedure the titanium base alloy may be held in the molten salt bath until it reaches the temperature of the salt, it is not necessary to do so; and a good coating may be obtained if the titanium alloy part is retained in the salt until it reaches the melting point of the salt. That is, if it is desired to do so, it may be held in the salt a period of time sufficient to prevent the salt to become molten on the surfaces of the titanium base alloy part after the initial solidification of the salt layer thereon.

These alternative procedures, however, are normally not as desirable as the preferred procedure as described inasmuch as they afford a greater opportunity for oxides to form on the surface of the titanium part. Moreover, the preferred procedure eliminates the tendency to build up an uneven salt layer which is thicker on large sections and thinner on small sections of the part to be coated. Although these alternative procedures reduce the length of time it is necessary to hold the titanium base alloy in the molten aluminum, as compared with the preferred procedure hereinbefore described, they afford no additional advantages over the preferred procedure and require longer holding periods in the salt bath and a deeper layer of the molten salt flux. Hence, it is preferable to immerse the titanium or titanium base alloy part in the molten aluminum coating material immediately after it has contacted the salt bath and before the latter has remelted on the titanium base alloy part. In this manner a very adherent coating of aluminum or aluminum base alloy may be obtained.

It is also possible to obtain a satisfactory coating of aluminum on a titanium base alloy part by heating the latter in the activated fused salt bath until it reaches a temperature above the melting point of the aluminum coating metal and then allowing the titanium base alloy and coating of said salt thereon to cool to some tempera-
ture below the melting point of the aluminum or salt before immersion in the molten aluminum or aluminum base alloy coating bath. This procedure is satisfactory so long as the salt coating, if allowed to solidify on the titanium base alloy part, is not cracked or broken prior to immersion in the molten aluminum or aluminum base alloy coating bath and the molten titanium base alloy is permitted to remain in this coating bath for a time and at a temperature sufficient to reheat the surfaces of the titanium part and the salt coating to a temperature above the melting point of the aluminum coating metal and preferably to at least 1250° F. Satisfactory coating is obtained on the titanium base alloy parts may also be obtained by heating the latter in the molten salt bath maintained at a temperature below that of the molten aluminum or aluminum base alloy and, while the salt coating on the titanium base metal part is still molten, subsequently immersing the part and salt coating in the coating metal bath and heating the same to a temperature within the range of approximately 1200° F. to 1600° F.

The titanium or titanium base alloy part may be preheated, if desired before being immersed in the fused salt bath. This preheating treatment permits smaller quantities of salt and smaller sized salt bath heating means to be used than are necessary where the titanium alloy part is heated in the molten salt. If the preheating step is employed, it is preferable to heat the metal to be coated under such conditions that the surface thereof is not oxidized. An inert or reducing atmosphere furnace, such as one employing dried and purified helium or argon, may be used for this purpose. The preheating temperature is preferably within the range of approximately 1200° F. and 1600° F.

When the titanium or titanium base alloy part is preheated in a nonoxidizing atmosphere to the temperature of the fused salt bath and is free of oxides of titanium and other foreign matter, the time of immersion in the salt bath, as in the first-mentioned preferred procedure, may be as little as one or two seconds if the parts are free of complicated recesses. More complicated shapes may require a longer time in order to insure that the fused salt thoroughly covers the part to be coated with aluminum or aluminum alloy. Where the titanium or titanium base alloy part has titanium oxides on its surfaces, longer periods of immersion in the salt bath will be required in order to provide clean titanium surfaces. Of course, when the preheating step is not employed, sufficient time is required for either the fused salt or the aluminum coating metal bath to bring the titanium base alloy part to a temperature at least as high as, and preferably somewhat above, the melting point of the aluminum coating material. This time will, of course, depend on the dimensions of the titanium alloy and on the size and thermal efficiency of the salt bath. Retaining the titanium base alloy in the fused salt for extended periods of time has no detrimental effects on the resultant product.

The time of immersion in the molten aluminum or aluminum base alloy bath may vary from as little as one or two seconds up to several minutes, depending on which of the above procedures is selected and on the degree of complication of recesses, etc., in the parts being processed. However, insomuch as titanium and titanium base alloys are generally not readily soluble in aluminum and aluminum base alloys and do not form a low melting eutectic at the titanium and aluminum interface, they may be retained in the molten aluminum for considerable periods of time, if it is found convenient to do so.

If desired, separate containers and heating means may be employed for the salt bath and the coating metal bath but, in order to provide for activation of the fused salt bath by aluminum in or in contact with it, Where the fused salt is on top of the molten aluminum or aluminum base alloy, as described above, the proper activity of the molten salt is automatically obtained. On the other hand, where a separate bath and a separate aluminum or aluminum base alloy coating bath are employed, it is essential to activate the fused salt. This may be accomplished by employing an aluminum or aluminum alloy coated container for the fused salt, or aluminum or an aluminum alloy may be added to the salt. The aluminum or aluminum alloy may be added by immersing a bar or sheet of the metal in a fused salt bath. Such a bar or sheet readily melts and settles to the bottom of the salt bath. In general, however, it is preferable to have both the fused salt and the molten aluminum coating metal in a single furnace and, after fluxing in the molten salt bath, to immerse the titanium base alloy in the aluminum coating metal beneath the molten salt without transfer through air to a separate pot of molten aluminum. Such a procedure greatly reduces the possibility of having oxides formed on the surface of the titanium alloy part.

Various changes and modifications of the embodiments of my invention described herein may be made by those skilled in the art without departing from the principles and scope of the present invention, as set forth in the following claims:

1. A method of coating titanium and titanium base alloys with a coating metal of a class consisting of aluminum and aluminum base alloys which comprises immersing the titanium metal in a fused salt bath activated by aluminum in contact therewith, subsequently immersing the titanium metal in a molten bath of said coating metal, and thereafter removing the coated titanium metal from said coating bath.

2. A method as in claim 1 in which the fused salt bath is maintained at a temperature within the range of approximately 1200° F. to 1600° F.

3. A method as in claim 1 in which the temperature of the surface of the titanium metal is at least as high as the melting point of the coating metal while immersed therein.

4. A method of coating an article formed from a metal of a class consisting of titanium and titanium base alloys with a coating metal of a class consisting of aluminum and aluminum base alloys which comprises immersing the titanium base article in a fused salt bath comprising, by weight, approximately 37% to 57% KCl, 25% to 45% NaCl, 8% to 20% NaAlF₄ and 0.5% to 12% AlF₃, said fused salt bath being activated by aluminum in contact therewith, subsequently immersing the titanium base article in a molten bath of said coating metal, and thereafter removing the coated article from said metal coating bath, thereby forming a continuous interface chemical bond between the aluminum coating and titanium.

5. A method as in claim 4 which includes the step of removing excess coating metal from the coated article after removal from the coating bath and before the coating metal on the article has completely solidified.

6. A method as in claim 4 in which separate salt and coating baths are employed and the article is quickly transferred to the coating bath and then heated from room temperature to a temperature at least as high as the melting point of the coating metal while immersed therein.

7. The method of coating a titanium base alloy with a coating metal of a class consisting of aluminum and aluminum base alloys which comprises immersing the titanium base alloy in a fused salt bath comprising, by weight, approximately 37% to 57% KCl, 25% to 45% NaCl, 8% to 20% NaAlF₄ and 0.5% to 12% AlF₃ said fused salt bath being at a temperature within the range of approximately 1200° F. to 1600° F. and floating on top of a molten bath of said coating metal, said titanium base alloy being retained in said fused salt for an insufficient period of time to raise the temperature of said titanium base alloy to the temperature of said salt, subsequently
lowering the titanium base alloy into the molten coating metal bath, and thereafter removing the coated titanium base alloy through the said fused salt.

8. A method as in claim 7 which includes the step of removing excess coating metal from the titanium base alloy after removal of the titanium base alloy from the coating metal bath and before the coating on the titanium base alloy has completely solidified.

9. A method as in claim 7 in which the fused salt bath is maintained at a temperature between approximately 1300°F and 1400°F.

10. The method of treating an article formed of an alloy of the class consisting of titanium and titanium base alloys preparatory to coating the same with a metal of the class consisting of aluminum and aluminum base alloys which includes immersing the article in a molten salt bath comprising, by weight, approximately 37% to 57% KCl, 25% to 45% NaCl, 8% to 20% Na₃AlF₆ and 0.5% to 12% AlF₃, said molten salt bath being maintained at a temperature within the range of approximately 1200°F to 1600°F, while the article is passing therethrough.

11. The method of coating an article formed from a metal which contains at least 50% titanium with a coating metal containing at least 80% aluminum to form a continuous chemical bond between said titanium and aluminum coating metal, said method comprising passing said article into and out of said coating metal bath through a molten salt layer floating on said molten coating metal bath, said article being passed through said salt layer into said coating metal bath sufficiently quickly so that the salt solidifies on said article and does not remelt until immersed in said coating metal bath, said molten salt layer consisting essentially of 37% to 57% by weight of KCl, 25% to 45% by weight of NaCl, 8% to 20% by weight of Na₃AlF₆ and 0.5% to 12% by weight of AlF₃, said molten salt layer being maintained at a temperature of approximately 1200°F to 1600°F, while the article is passing therethrough.

12. A method as in claim 11 in which the article is retained in the coating metal until the surfaces of said article reach a temperature equal to at least the melting point of said coating metal.

13. A method as in claim 11 which includes the step of removing excess coating metal from the article after removal of the article from the coating metal bath and before the coating on the article has completely solidified, thereby forming a relatively thin coating on the article.

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